

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 5.00

Microfiche (MF) 65

ff 653 July 65

FACILITY FORM 802

N68-22707
(ACCESSION NUMBER) (THRU)

14 (PAGES) 1 (CODE)
01#44353 (NASA CR OR TMX OR AD NUMBER) 18 (CATEGORY)

SEPARATOR DEVELOPMENT PHASE OF HEAT-STERILIZABLE
BATTERY DEVELOPMENT PROGRAM
(BATTERY CASE DEVELOPMENT)

FINAL REPORT
15 February 1968

Contract No. 951091
(NAS 7-100)
Supplement No. 2

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This work was performed for the Jet Propulsion Laboratory,
California Institute of Technology, sponsored by the
National Aeronautics and Space Administration under
Contract NAS7-100.

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FOREWORD

This report was prepared by Whittaker Corporation, Narmco Research & Development Division, under Contract No. 951091 (NAS 7-100), entitled "Separator Development Phase of Heat Sterilizable Battery Development Program (Battery Case Development)," for the Jet Propulsion Laboratory of the California Institute of Technology. The program was accomplished under the direction of Mr. Werner von Hartmann, Project Officer. The research work was conducted in Narmco's laboratory by Mr. Floyd D. Trischler, Senior Chemist, and Mr. William Warner, Technician. Mr. Floyd D. Trischler served as Program Manager and Mr. Harold H. Levine as Staff Scientist. This report covers the period from 10 April 1967 to 31 January 1968.

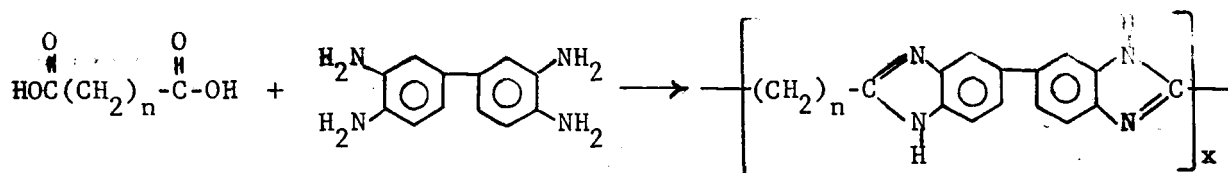
SUMMARY

The objective of this program was the development of an injection-moldable polymer suitable for use as the case in heat sterilizable batteries. The polybenzimidazole studied, which was based on diamino-benzidine and sebacic acid (PBI-8), met all of the preliminary requirements for the battery case. Some bonds were made with the aid of epoxy adhesives. Solvent welding was found to be the best method to join the PBI-8 polymer. A capped PBI-8 was extruded and injection molded. A number of injection-molded tensile specimens were prepared and tested.

DISCUSSION

Heterocyclic polymers are noted for their thermal and chemical stability. It was believed that thermoplastic polymers of this type would be ideal as the case material in a heat sterilizable battery.

Aliphatic polybenzimidazoles are prepared by the condensation polymerization of an aliphatic dibasic acid with an aromatic tetraamine as follows:



Theoretically, there are no groups present in the polymer which should be affected by potassium hydroxide.

The suberic acid based polybenzimidazole and the sebacic acid based polybenzimidazole (PBI-8) were given a preliminary evaluation as a heat sterilizable battery case material. The PBI-8 polymer was selected as the most likely candidate because of its ease of processing and lower raw material cost.

PBI-8 polymers were prepared which had inherent viscosities ranging from 0.58 to 1.51. The optimum viscosity range for compression molding of this polymer was found to be from 0.8 to 1.3. If the inherent viscosity is over 1.33, the polymer has too high a molecular weight to obtain sufficient flow. The polymer degrades if held at 605°F for any extended period of time. The results of this study are summarized in Table I.

TABLE I
COMPRESSION MOLDABILITY OF PBI-8

Inherent Viscosity	Polymer Fusion Temp @ 1000 psi, °F	Remarks
0.58	490	--
0.84	550	--
1.04	555	--
1.33	587	--
1.67	>605	Degradation occurs about 605°F
1.95	>605	Degradation occurs about 605°F

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Several molded bars were subjected to stress and sterilized in the stressed position. There was no tendency of the molded piece to crack or craze.

An attempt was made to run the Brabender viscosity of the sebacic and suberic acid based PBI's. The temperature in the viscometer could not be increased above 730°F, and the polymer viscosity was too high for that type of viscometer.

Since the PBI-8 polymer passed all of the preliminary experiments for a sterilizable battery case, various methods of bonding strips of the polymer together were investigated. Heat pressure fusion, electrical resistance tape, and thermoplastic welding were investigated. These techniques were found to be unsatisfactory due to blowing of the joints.

Solvent joining was also investigated as a bonding technique. The solvent joining method consisted of laying one-half of the joint on double-sided masking tape, one side of which was bonded to a flat board. The joints were moistened with solvent, and the other half of the joint was laid on top of the first half. The masking tape prevented movement of the parts during assembly. A metal bar was then laid across the top and bottom of the joint. Pressure was applied by tightening two C-clamps, one on each end of the bar. The solvent was then removed at various drying cycles, then the unit was disassembled.

Various chemicals were investigated as potential candidates for solvent welding the PBI-8, but only formic acid (FA) was found effective. Since difficulties were encountered in removing all of the FA from the bonds, mixtures of FA and diluents were examined. A mixture of 20% FA-80% dimethylformamide (DMF) showed the most promise.

Satisfactory bonds could not be obtained from a conventional relief-milled lap joint or a 45° scarfed joint due to stresses in the adherend. Therefore, a new type of lap joint was designed and is shown in Figure 1. This new joint was found to be superior to all previous joints, and had no inherent weaknesses.

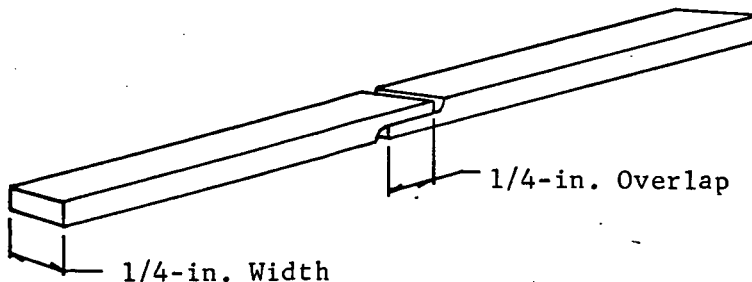


Figure 1. New Type of Lap Joint

Solvent-welded bonds were prepared using the new joint design resulting in excellent joints in which the adherend failed rather than the bond. The bond strength was relatively unaffected when tested at 135°C after sterilization. The data are compiled in Table IV.

In the preliminary extrusion study with the PBI-8, problems were encountered when the polymer advanced in the extruder, resulting in screw seizure. In order to prevent polymer advancement during processing, several alternative methods of capping the PBI-8 polymer were studied. One of the methods tried was to use excess sebacic acid. As shown in Table V, excess sebacic acid results in a cross-linked polymer, with the crosslink density increasing proportionately with the excess sebacic acid.

TABLE IV

**BONDING RESULTS FOR NEW RELIEF-MILLED
MOLDED PBI-8 LAP JOINTS**

Bonding Method*	Tensile Shear Strength, psi		
	RT	RT after Sterilization	135°C after Sterilization
Solvent welded, 20% FA/DMF	> 1730**	> 1625**	> 1540**

* PBI-8: Molding grade, inherent viscosity 0.85
FA: Formic acid
DMF: Dimethylformamide

** Adherend failure.

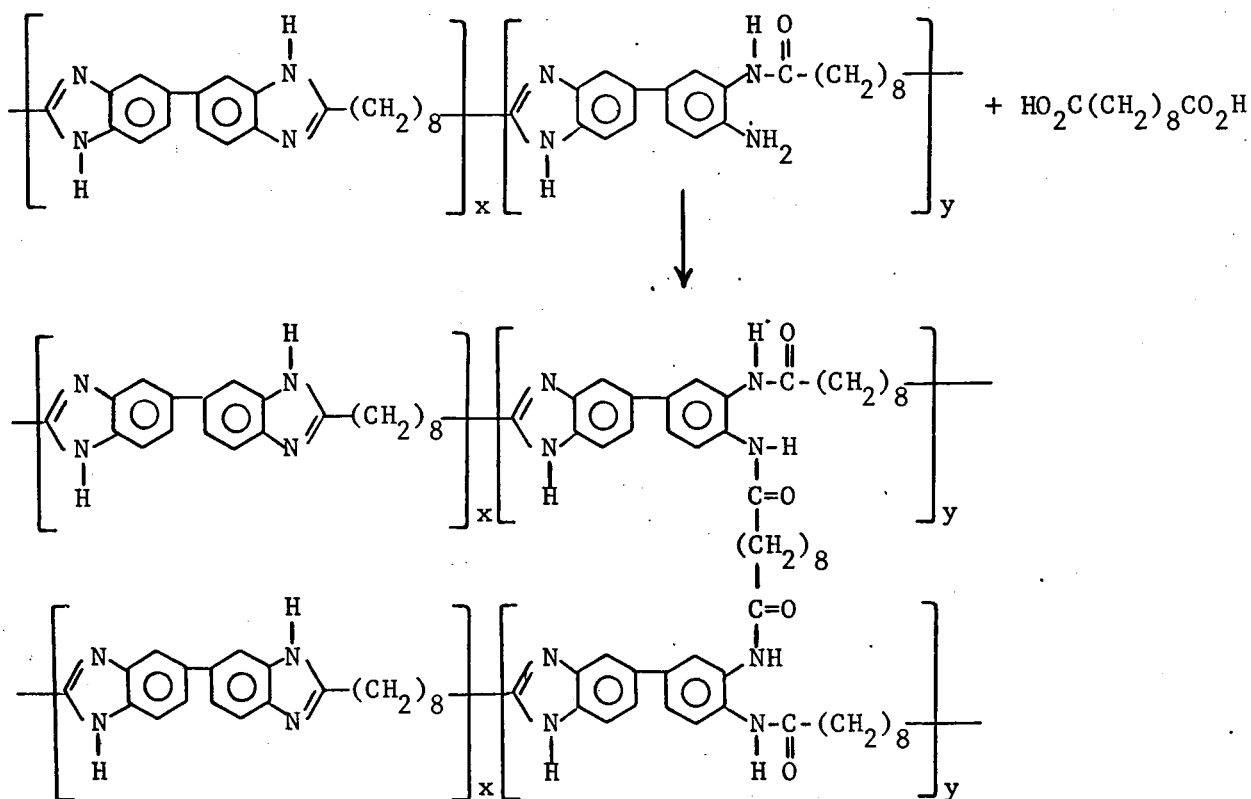
NOTE: The solvent welded joints were heated under vacuum for 30 min @ RT, 3 hr @ 100°C, and 16 hr @ 135°C, to remove the solvent.

TABLE V

EFFECT OF EXCESS SEBACIC ACID ON PBI-8

Moles Sebacic Acid: Moles Diaminobenzidine	Inherent Viscosity after 1-hr Advancement @ 600°F	Inherent Viscosity after 3-hr Advancement @ 600°F
1.0000:1.0000	0.50	--
1.0100:1.0000	0.69	Insoluble and infusible ↓
1.0256:1.0000	1.16	
1.0526:1.0000	Insoluble and infusible	
1.1111:1.0000	Insoluble and infusible	

The crosslinking is believed to be a result of amide formation through unclosed benzimidazole rings, as shown in the following reaction scheme.



Phenyl benzoate as well as excess diaminobenzidine (DAB) was found to be effective in capping the PBI-8 polymer (Table VI).

TABLE VI

EFFECT OF PHENYL BENZOATE OR EXCESS DIAMINO BENZIDINE ON PBI-8

Moles Diaminobenzidine: Moles Sebacic Acid	Inherent Viscosity after 1-hr Advancement @ 600°F	Inherent Viscosity after 3-hr Advancement @ 600°F
1.0526:1.0000	0.48	0.55
1.0256:1.0000	0.70	0.94
1.0100:1.0000	0.85	1.21
1.0000:1.0000 + 0.0526 Phenyl benzoate	0.63	0.78

It was found that 1.0 to 2.6 mole percent excess DAB is needed to produce PBI-8 polymer which is satisfactory for extruding without advancement

during processing. The resultant polymer has an inherent viscosity in the range from 0.7 to 1.2. A greater amount of DAB results in a polymer which has too low a molecular weight, while a lesser amount results in a polymer which has too high a molecular weight and cannot be processed satisfactorily.

The original method of producing PBI-8 polymer was limited to 2-1/2 lb for each run. The process involved preparing a prepolymer which solidified in the reaction vessel and, after cooling, scraping it from the reaction vessel. The prepolymer was then placed in trays and advanced in an oven. The quantity of prepolymer which can be prepared is limited, however, since it foams immediately before solidification.

A new production method was devised whereby the prepolymer is prepared and poured into large trays while in the molten state. The prepolymer is then advanced in an oven. By using this method, 10 pounds of polymer were prepared in a single run.

The relationship between the polymer fusion temperature and the extrusion temperature was determined for polycarbonate and related to the PBI-8 polymer. The temperature differential between the fusion temperature and the extrusion temperature was found for polycarbonates and polysulfones. This temperature differential was then added to the polymer fusion temperature of the PBI-8 in order to have a starting point for the extrusion study. It was found that the extrusion temperature is 75°-90°F above the polymer fusion temperature, as shown in Table VII. The capped PBI-8 can be extruded into rods and sheets at 650°F.

TABLE VII

EXTRUSION AND POLYMER FUSION TEMPERATURES
OF THE CAPPED PBI-8 POLYMER

Polymer Inherent Viscosity	Polymer Fusion Temp, °F	Extrusion Temp,* °F
Polycarbonate	370	460, 500**
0.94	575	650
1.21	600	680
Polysulfone	--	580

* Extruder barrel temperature.

** Back and front barrel temperature, respectively.

The injection molding feasibility study was conducted in a 1/2 oz to 1-1/2 oz Van Dorn machine. The parameters governing the molding of tensile specimens (as per ASTM P638-61T, Type I 1/8 in. thick) are listed below.

1. Nozzle size: 5/32-in. diameter
2. Sprue size: 7/32 - 13/32 in. diameter
3. Runner size: 1/4-in. depth by 13/32-in. width
4. Gate size and location: 5° trapezoid at end of tensile bar
5. Mold temperature: 380°-400°F
6. Mold closed (cooling rate): 25 seconds
7. Injection pressure: 1900 psi gauge (15,000 psi material)
8. Compression ratio (Feed Volume:Part Volume): 4:1
9. Recommended resin drying time: Overnight at 275°F in a
circulating air oven or
4 hours at 275°F in a
vacuum oven
10. Cylinder temperature: 640°-660°F
11. Nozzle temperature: 610°-620°F
12. Rate of feed of polymer: 4-1/2 lb/hr
13. Total molding cycle: 52 seconds
14. Regrind life: >2 regrinds
15. Hopper temperature: 280°F
16. Molding cycle: Injector Forward: 20 seconds
Prepack: 7 seconds
Mold Closed: 25 seconds

When molding the PBI-8 polymer, a heated hopper is recommended for minimizing moisture pickup.

Since the cylinder temperature required is so high, frequent purging of the chamber is recommended, particularly if the molding cycle is interrupted for any period of time.

Aerosol Plastic Mold Spray and Silicon Mold Release were found to be excellent mold release agents for injection molding the PBI-8 polymer.

The tensile strengths of the injection molded specimens were in excess of 10,000 psi, with heat annealing offering no improvement.

Single lap, double lap and machined solvent-welded joints were prepared from the injection molded PBI-8 polymer using a 20% FA/80% DMF. In all

cases, the adherend failed rather than the joint. Sterilization had no apparent effect on the bond strength.

Several epoxy resins were evaluated as adhesives for the injection molded PBI-8. These included DEN 438EK85, Epon 828, DEN 438 and ERL 0510, all cured with 5% DMP 30. The surface was roughened by sandblasting and a uniform 2-mil bondline was obtained.

The adhesive consisting of 1/2 DEN 438 and 1/2 ERL 0510 was found to be equivalent to DEN 438EK85. In both systems, the adherend failed at a tensile shear of >1400 psi. The system using 1/2 DEN 438 and 1/2 ERL 0510 would appear to be preferable since it contains no solvent which has to be removed.

CONCLUSIONS AND RECOMMENDATIONS

The injection molded PBI-8 polymer meets all of the preliminary requirements for a heat sterilizable silver-zinc battery case. This polymer is not affected by the electrolyte, can be readily bonded, and is not sensitive to stress cracking. While most of the bonding has been performed by solvent welding, sufficient bonds have been prepared from epoxy adhesives to demonstrate their feasibility.

It is recommended that a limited number of battery cases be made from the PBI-8 polymer, assembled and given a preliminary pressure testing and evaluation. Should these tests prove satisfactory, a sufficient number of batteries should be prepared for a full evaluation.